Kinetics of the Dissociation of Iron(II) Porphyrin Oxygen Adducts. Axial Base Effects

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Summary The displacement of oxygen from Fe(TPP)-(base)(O_2) is a dissociative process in which the axial base exerts a *trans* effect with the lability of the co-ordinated oxygen decreasing in the order pyridine > piperidine >> 1-methylimidazole.

WE have recently prepared and characterized molecular oxygen adducts of some simple iron(II) porphyrins in CH_2Cl_2 at -79 °.[1] In addition, other iron complexes have been prepared which react reversibly with oxygen both at low temperatures[2] and at room temperature.[3] However,

no quantitative study of oxygen binding to iron complexes has yet been reported. Conversely, oxygen binding to cobalt complexes has been extensively studied,[4] and carbon monoxide binding to iron phthalocyanines was recently investigated.[5] In these systems the bonding properties of the axial base were found significantly to influence the binding of small molecules *trans* to that base. Consequently, we have examined reaction (1) as a possible model

$$Fe(TPP)(base)(O_2) + base \rightarrow Fe(TPP)(base)_2 + O_2 \quad (1)$$

for myoglobin and hemoglobin, in hopes of determining the properties of the axial base which most influence the binding of oxygen to the heme.

TABLE

Kinetic data for the reaction of Fe(TPP)(B)(O_2)[a] and excess of base in CH_2Cl_2 at −79 °C. py = pyridine, pip = piperidine Meim = 1-methylimidazole.

	Base, B	[B]/M	$10^3 \times k_{obs}$[b]/s^{-1}
Fe(TPP)(py)(O_2) ..	py	0·05	4·3
" ..	"	0·13	4·5
" ..	"	0·19	4·3
" ..	"	0·24	4·4
Fe(TPP)(pip)(O_2) ..	pip	0·41	2·3
" ..	"	0·47	2·5
" ..	"	0·59	2·1
Fe(TPP)(Meim)(O_2) ..	Meim	0·04	0·19
" ..	"	0·11	0·17
" ..	"	0·20	0·17

[a] [Fe(TPP)(B)(O_2)] = (2·6—6·6) × 10^{-5} M; 1 atm O_2. [b] Estimated error ± 5%. [c] Range of piperidine concentrations limited by large [piperidine] required to displace oxygen from Fe(TPP)(pip)(O_2).

We have investigated the six-co-ordinate oxygen adducts Fe(TPP)(B)(O_2) (TPP = tetraphenylporphyrin, B = pyridine, piperidine, and 1-methylimidazole), which were prepared as previously described.[1] Oxygen displacement was initiated by adding excess of base to the solutions containing Fe(TPP)(B)(O_2). Concentrations of oxygen and base in solution were always in a large excess compared to that of the porphyrin complexes. The kinetics were studied at −79 °C in oxygen-saturated (1 atm) CH_2Cl_2. The decay of the peak at 547 nm (characteristic of the oxygen adduct)[1] was followed on a Cary 14 spectrometer using a Pyrex cell.[4c] In all cases $-d[Fe(TPP)(B)(O_2)]/dt$ was first order for more than 3 half-lives. The kinetic data, summarized in the Table, show that for a given complex the observed rate constant, k_{obs}, is independent of the base concentration. Such evidence is indicative of a dissociative mechanism in which the oxygen adduct forms a five-co-ordinate intermediate, Fe(TPP)(B), prior to forming the six-co-ordinate product, $Fe(TPP)(B)_2$. Hence, k_{obs} is a measure of the

$$Fe(TPP)(base)O_2 \xrightarrow{k_{obs}} Fe(TPP)(base) + O_2$$

$$Fe(TPP)(base) + base \xrightarrow{fast} Fe(TPP)(base)_2$$

lability of the co-ordination oxygen.

The data in the Table reveal that no simple correlation exists between k_{obs} and pK_a of the protonated axial base [pK_a(py) = 5·27[6] pK_a (pip) = 11·30,[6] pK_a (Meim) = 7·25].[7] When 1-methylimidazole is the axial base, the lability of O_2 is significantly less than that observed when pyridine or piperidine occupies the same position. This is particularly interesting if one considers that in the heme protein the axial ligand is an imidazole of the globin. The iron–oxygen bond has been explained[8] in terms of a σ-bond from oxygen to iron and a $d\pi \rightarrow p\pi$-bond from iron to oxygen. Within this model, the ligand *trans* to O_2 will compete for the π-electron density on the iron. Therefore, the lability of O_2 will be sensitive to the π-donor properties of the axial base. Imidazole is believed to be a better π-donor than pyridine,[9,10] whereas piperidine is a saturated amine. Hence, the decreased lability of the O_2 *trans* to the 1-methylimidazole may reflect the better π-donor properties of this axial base. Enhanced oxygen binding to cobalt complexes with 1-methylimidazole in the *trans* position,[4] as well as enhanced CO binding to iron phthalocyanines with imidazole as the axial base,[5] have been attributed to its π-donor effect.

However, the relative order of oxygen lability in Fe(TPP)(pip)(O_2) *vs.* Fe(TPP)(py)(O_2) indicates that a strong σ-donor can overcome the effect of a moderate π-donor. It is interesting that this order for piperidine and pyridine complexes is opposite to that observed by Stynes and James[5] for the bonding of CO to iron phthalocyanine complexes. This may reflect different modes of bonding[8] for CO and O_2 in the respective systems (perhaps a linear CO adduct *vs.* a bent O_2 adduct),

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